

**PROCESS FOR THE GASIFICATION OF ORGANIC
MATERIALS, PROCESSES FOR THE GASIFICATION OF
CLASS FIBER REINFORCED PLASTICS, AND APPARATUS**

Related Applications

00 1. This application is a divisional application of application Serial No. 08/872,201 filed June 10, 1997 (now abandoned), which is a continuation-in-part of application Serial No. 08/748,116 filed November 12, 1996 (now abandoned) which, in turn, is a continuation of application Serial No. 08/324,310, filed October 17, 1994 (now abandoned). ✓

BACKGROUND OF THE INVENTION

00 2. This invention relates to a process for burning or gasifying an organic material through partial oxidation and thereby producing an effectively utilizable gas. ✓

00 3. Conventionally, organic materials including wood, farm products (such as sugarcane and corn), common plants (such as algae and weeds) and the like have been gasified. Moreover, techniques for the gasification of waste products consisting largely of organic materials have recently been developed for the purpose of processing industrial waste including plastics, waste paper, so- ✓

called shredder dust obtained by crushing plastics in scrapped automobiles, scrapped FRP boats composed mainly of thermoset resin, and the like.

00 4. Generally, conventional processes for the gasification of such organic materials have been carried out in a single-stage pyrolysis or combustion furnace of the moving bed or fluidized bed type using air or oxygen, for the main purpose of recovering waste heat. Recently, processes for thermally decomposing plastics-containing waste in a single-stage pyrolysis furnace to recover its oil content are also being developed.

00 5. Each of the above-described conventional processes involves the following problems.

(1) Pyrolysis

00 6. Plastics: Since a plurality of materials are mixed together, the pyrolysis temperature varies widely from about 300°C to 800°C, thus making the operation difficult. Moreover, the formation of soot due to undecomposed carbon and the deposition of coking products on the walls of the apparatus are problematic. Furthermore, since the pyrolytically produced oil has poor quality because of the inclusion of such undecomposed carbon, it can only be used as a low-quality fuel oil.

00 7. Wood, farm products, common plants (e.g., algae and weeds) and the like: About 40 to 60% of residual carbon is formed. Moreover, the pyrolysis gas has a high CO₂ content and hence a low calorific value, it cannot be used as a fuel gas. ✓

00 8. Shredder dust: This material involves the same problems as described above in connection with plastics. ✓

(2) Combustion with the aid of air. ✓

00 9. ~~(a)~~ The exhaust gas resulting from combustion is composed mainly of N₂ and CO₂ and, therefore, cannot be used as fuel because of its very low calorific value.

00 10. ~~(b)~~ Soot and NO_x are formed as by-products. Moreover, the problem of secondary environmental pollution, for example, due to the formation of dioxin and its analogues may arise. ✓

011. ~~(c)~~ Especially in the case of plastics, their combustion produces high temperatures exceeding about 1,200°C and hence tends to cause damage to the walls of the combustion furnace. ✓

Ø12. The present invention also relates to processes and apparatus for effectively utilizing glass fiber reinforced plastic (GFRP) waste by the gasification thereof. More particularly, it relates to a process and apparatus for gasifying GFRP waste to produce a gas utilizable as a synthesis gas, as well as a process and apparatus for gasifying GFRP waste to recover the heat so generated. ✓

Ø13. In addition to the above-described problems, the gasification of GFRP involves another problem. That is, the plastic component of GFRP tends to undergo coking because the inside of the GFRP is heated to a high temperature as a result of its combustion reaction with oxygen and the rapid oxygen consumption causes a shortage of oxygen, thus making it difficult to gasify the plastic component completely. ✓

Ø14. Consequently, it is impossible to isolate the glass fibers and utilize them effectively. ✓

SUMMARY OF THE INVENTION

Ø15. It is an object of the present invention to provide a process for the gasification of an organic material which can prevent the presence of residual unreacted carbon and the formation of soot by incomplete combustion during gasification of the organic material and thereby makes it possible to produce a ✓

high-quality gas or recover energy with high efficiency. This object is accomplished by a first embodiment of the present invention.

Ø 16. The first embodiment of the present invention involves the following means: ✓
✓

~~(1)~~ (i) Air or oxygen is used as an oxidizing agent.

~~(2)~~ (ii) An oxidation reaction and a water gas reaction are made to take place concurrently. ✓

~~(3)~~ (iii) The process is carried out so that the molar ratio (H_2O/C) of the supplied steam to the carbon in the organic material is in the range of 1 to 10, in particular in the range of 2 to 10, and specifically, in the range of 2 to 5. ✓

Ø 17. According to the first embodiment of the present invention which is provided with the above-described means, an organic material is processed as follows: ✓

~~(1)~~ Partial oxidation

Ø 18. As an oxidizing agent, air (or oxygen) has conventionally been used in an excessive amount greater than the stoichiometric amount required for ✓

combustion. In this case, when an organic material is burned (or oxidized) by reaction with oxygen in the air, oxygen provides such a high combustion rate that the surface of the organic material is first burned with the consumption of oxygen. Thereafter, oxygen is supplied to the surface of the organic material by diffusion, but the oxygen supply becomes insufficient because the diffusion rate is lower than the combustion rate. As a result, nitrogen remains on the surface of the organic material and a shortage of oxygen occurs locally on the other hand, the surface of the organic material becomes hot as a result of the combustion caused by oxygen. However, no combustion reaction takes place because of the shortage of oxygen, and only the condensation reaction of carbonaceous materials leads to the formation of soot. If chlorine is present in the combustion gas, this soot reacts with chlorine to form harmful substances (i.e., dioxin and its analogues) as by-products. Moreover, the shortage of oxygen also results in the formation of NO_x. The above-described problems can be solved by suppressing the supply of air (or oxygen) so as to supply only the amount of oxygen required to maintain a temperature of 700 to 900°C and, thereby, keep the reaction temperature constant through a so-called partial oxidation reaction.

(2) 0/9. An oxidation reaction and a water gas reaction are made to take place concurrently. ✓

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19. The oxidation reaction is an exothermic reaction, whereas the water gas reaction is an endothermic reaction. Accordingly, the reactions can be allowed to proceed gently by making both of them take place concurrently. Thus, the formation of soot and NO_x due to a runaway of the oxidation reaction as described above in (1) can be prevented. ✓

Oxidation reaction



Water gas reaction



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(3) The molar ratio of the supplied steam to the carbon in the organic material is regulated. ✓

020. The partial oxidation reaction is an exothermic reaction, whereas the water gas reaction is an endothermic reaction. Accordingly, the amount of heat absorbed increases with the amount of H_2O supplied, and the temperature is lowered when the amount of heat absorbed exceeds the amount of heat generated in the oxidation reaction. For the gasification temperature, a proper range exists for the following reasons. ✓

023 (a) At 700°C or below, unreacted materials are formed as a tarry by-product. ✓

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22. (b) At 900°C or above, the polymerization or condensation reaction of carbonaceous materials is promoted owing to a sharp rise in temperature, and the diffusion of oxygen required for combustion is delayed, so that soot is formed as a by-product. Thus, in order to maintain any proper gasification temperature (in the range of 700 to 900°C), there exists a proper range of the H_2O/C ratio. ✓

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23. This proper value for H_2O/C varies according to the type of the organic material. For example, organic materials having a high oxygen content (e.g., polyurethanes, biological materials and paper) require a larger amount of H_2O than organic materials containing no oxygen (e.g., polyethylene and polypropylene). For organic materials (e.g., FRP) containing a large amount of ash (or inorganic components), a small amount of H_2O is sufficient (see Table 1). ✓

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24. On the basis of equilibrium calculations, the molar H_2O/C ratio is preferably in the range of 2 to 5, though it depends on the particular organic material. However, with consideration for the degree of utilization of H_2O as defined by channeling or the like according to the geometry of the gasification ✓

furnace (of the fluidized bed, spouted bed, kiln or moving bed type), a molar H_2O/C ratio in the range of 2 to 10 is generally used.

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-25. Where CO is produced according to the following reaction (3) instead of completely burning the carbon in the organic material to form CO_2 , or where the amount of O_2 is reduced in order to suppress the combustion reaction (4) of H_2 in the product gas, the amount of H_2O supplied may be smaller. ✓



In these cases, the molar H_2O/C ratio is preferably in the range of 2 to 5.

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-26. Table 1 ✓

Element analysis of Organic materials (wt%)

| Organic material | C | H | O | N | Ash/ Water |
|------------------|------|------|------|-----|---------------|
| Polyethylene | 85.7 | 14.3 | 0.0 | 0.0 | 0.0 |
| Polypropylene | 85.8 | 14.2 | 0.0 | 0.0 | 0.0 |
| Polyurethane | 57.9 | 7.9 | 28.1 | 6.1 | 0.0 |
| FRP(*) | 50.4 | 4.4 | 7.5 | 0.0 | 37.7 |

| | | | | | |
|----------|------|-----|------|-----|------|
| Kaoliang | 42.5 | 5.7 | 41.4 | 0.0 | 10.4 |
| Paper | 36.5 | 5.0 | 40.9 | 0.0 | 17.6 |

(*) An unsaturated polyester resin for use in fishing boats

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27. In view of the above-described technological level of the art, it is another object of the present invention to provide a process and apparatus for gasifying the plastic component of GFRP, withdrawing the remaining glass fibers, and recovering useful components from the plastic gas produced by the gasification of the plastic component. This object is accomplished by second and third embodiments of the present invention.

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28. According to the second embodiment of the present invention, there is provided a process for the gasification of glass fiber reinforced plastics which comprises the first step of feeding a glass fiber reinforced plastic material to a gasification section, heating the material to a temperature of 650 to 750°C in the presence of oxygen and steam to gasify the plastic component thereof, and recovering the remaining glass fibers; and the second step of introducing the resulting plastic gas into a plastic gas decomposition section, partially oxidizing the plastic gas in the presence of additional oxygen or an additional mixture of oxygen and steam, and recovering the CO and H₂ so produced.

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29. According to the third embodiment of the present invention, there is provided an apparatus for the gasification of glass fiber reinforced plastics which comprises a gasification furnace consisting of a horizontally disposed rotatable cylindrical structure and having a heating zone for heating a glass fiber reinforced plastic material to a temperature of 650 to 750°C in the presence of oxygen and steam to gasify the plastic component thereof and a recovery zone for recovering the glass fibers remaining as a result of the heating; a plastic gas decomposition furnace connected to said gasification furnace and disposed vertically for partially oxidizing the plastic gas introduced from said gasification furnace at a temperature of 700 to 1,000°C in the presence of additional oxygen or an additional mixture of oxygen and steam; and a gas purification column for purifying the gas produced in said decomposition furnace to recover CO and H₂. ✓

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30. According to the second and third embodiments of the present invention, a GFRP material is processed as follows: ✓

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31. In the first step of the above-described process, the GFRP material is fed to a gasification section where it is heated to a temperature of 650 to 750°C in the presence of oxygen and steam. Thus, only the plastic component of the GFRP material is gasified completely. It is conceivable to use oxygen alone during this ✓

gasification, but this may produce high temperatures locally. Consequently, oxygen diluted with steam is used to ensure complete gasification. The gasification conditions in this first step are preferably such that the ratio of oxygen to GFRP is in the range of 0.09 to 0.50 N liter of oxygen per gram of GFRP and the ratio of steam to GFRP is not less than 2.0 grams of steam per gram of GFRP. The gas produced in the first step comprises CO, CO₂, H₂, O₂, methane, ethane, propane, and other hydrocarbon compounds having a boiling point ranging from room temperature to about 700°C. This gas will hereinafter be referred to as the plastic gas. Since the glass fibers have a melting point of about 830°C, they remain intact in the first step and are recovered in solid form.

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32. In the succeeding second step, the plastic gas from which the glass fibers were separated is transferred to a plastic gas decomposition section where it is partially oxidized in the presence of additional oxygen or an additional mixture of oxygen and steam. The combustion conditions in the second step are preferably such that, when the amount of the plastic gas is expressed in terms of the GFRP material, the ratio of oxygen to GFRP is in the range of 0.11 to 0.71 N liter of oxygen per gram of GFRP depending on the amount of oxygen used in the first step and, when steam is fed together with oxygen, the ratio of steam to GFRP is not less than 3.0 grams of steam per gram of GFRP. Then, the gas leaving the

plastic gas decomposition section is transferred to a gas purification column where it is purified for use as a synthesis gas.

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33. In view of the above-described technological level of the art, it is still another object of the present invention to provide a process and apparatus for gasifying the plastic component of GFRP, withdrawing the remaining glass fibers, and recovering the heat generated by the gasification of the plastic. This object is accomplished by fourth and fifth embodiments of the present invention. ✓

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34. According to the fourth embodiment of the present invention, there is provided a process for the gasification of glass fiber reinforced plastics which comprises the first step of feeding a glass fiber reinforced plastic material to a gasification section, heating the material to a temperature of 650 to 750°C in the presence of air and steam to gasify the plastic component thereof, and recovering the remaining glass fibers; and the second step of introducing the resulting plastic gas into a combustion section, burning the plastic gas at a temperature of 700 to 1,000°C in the presence of additional air or an additional mixture of air and steam, and recovering the heat so generated. ✓

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35. According to the fifth embodiment of the present invention, there is provided an apparatus for the gasification of glass fiber reinforced plastics which ✓

comprises a gasification furnace consisting of a horizontally disposed rotatable cylindrical structure and having a heating zone for heating a glass fiber reinforced plastic material to a temperature of 650° to 750°C in the presence of air and steam to gasify the plastic component thereof and a recovery zone for recovering the glass fibers remaining as a result of the heating; a combustion furnace connected to said gasification furnace and disposed vertically or burning the plastic gas introduced from said gasification furnace at a temperature of 700 to 1,000°C in the presence of additional air or an additional mixture of air and steam; and a heat recovery unit for recovering heat from the gas produced in said combustion furnace.

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36. According to the fourth and fifth embodiments of the present invention, a GFRP material is processed as follows: ✓

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37. In the first step of the above-described process, the GFRP material is fed to a gasification section where it is heated to a temperature of 650 to 750°C in the presence of air and steam. Thus, only the plastic component of the GFRP material is gasified completely. It is be conceivable to use air alone during this gasification, but this may produce high temperatures locally. Consequently, air diluted with steam is used to ensure complete gasification. The gasification ✓

conditions in this first step are preferably such that the ratio of air to GFRP is in the range of 0.4 to 2.4 N liters of air per gram of GFRP and the ratio of steam to GFRP is not less than 2.0 grams of steam per gram of GFRP. The gas produced in the first step comprises CO, CO₂, H₂, N₂, O₂, methane, ethane, propane, and other hydrocarbon compounds having a boiling point ranging from room temperature to about ⁷⁰⁰~~750~~°C. This gas will hereinafter be referred to as the plastic gas. Since the glass fibers have a melting point of about 830°C, they remain intact in the first step and are recovered in solid form. ✓

⁰⁴⁰₃₈. Then, the plastic gas from which the glass fibers were separated is transferred to a second step where it is burned in the presence of additional air or an additional mixture of air and steam, and the heat so generated is recovered. The combustion conditions in the second step are preferably such that, when the amount of the plastic gas is expressed in terms of the GFRP material, the ratio of air to GFRP is in the range 2 of 2.3 to 4.3 N liters of air per gram of GFRP depending on the amount of air used in the first step and, when steam is fed together with air, the ratio of steam to GFRP is not less than 3.0 grams of steam per gram of GFRP. ✓

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39. Further scope of applicability of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the invention will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

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40. The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of illustration only, and thus are not limitative of the present invention and wherein:

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41. Fig. 1 is a flow diagram illustrating the process for the gasification of GFRP in accordance with the second embodiment of the present invention;

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42. Fig. 2 is a schematic view illustrating the apparatus for the gasification of GFRP in accordance with the third embodiment of the present invention;

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Fig. 3 is a flow diagram illustrating the process for the gasification of GFRP in accordance with the fourth embodiment of the present invention; and

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Fig. 4 is a schematic view illustrating the apparatus for the gasification of GFRP in accordance with the fifth embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

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The effects which can be achieved by the first embodiment of the present invention are explained hereinbelow with reference to the following Testing Examples 1-4 and Comparative Examples 1-2.

Testing Example 1

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Gasification was carried out using an apparatus having the specifications given below. In this case, no unreacted carbon was contained in the product gas.

(1) Gasification furnace

Spouted bed type

100 mm (inner diameter) x 1,500 mm (height)

~~(2)~~ Operating conditions for gasification ✓

730°C, 1 atm.

~~(3)~~ Results of operation ✓

(a) Raw material: Polyethylene = 100 g/h

(b) $\text{H}_2\text{O}/\text{C} = 1.3$ (molar ratio)

(c) Amount of O_2 supplied

$\text{O}_2/\text{C} = 0.4$ (molar ratio)

(d) Product gas

Flow rate = 378 NI/h

Composition (vol. %): $\text{H}_2=41$, $\text{CO} = 26$, $\text{CO}_2 = 26$, $\text{CH}_4 = 7$

(e) Rate of gasification: 100%

Testing Example 2

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Using the same apparatus as in Testing Example 1, gasification was carried out under the conditions given below. In this case, no unreacted carbon was contained in the product gas. ✓

~~(1)~~ Gasification furnace ✓

Spouted bed type

100 mm (inner diameter) x 1,500 mm (height)

~~(2)~~ Operating conditions for gasification ✓

760°C, 1 atm

~~(3)~~ Results of operation ✓

(a) Raw material: FRP (see Table 1) = 100 g/h

(b) $H_2O/C = 1.0$ (molar ratio)

(c) Amount of O_2 supplied

$O_2/C = 0.3$ (molar ratio)

(d) Product gas

Flow rate = 158 Nl/h

Composition (vol. %): $H_2 = 41$, $CO = 31$, $CO_2 = 26$, $CH_4 = 2$

(e) Rate of gasification: 100%

Comparative Example 1

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~~48.~~ Using the same apparatus as in Testing Example 1, gasification was carried out under the conditions given below. In this case, the temperature of the gasification furnace could not be kept above 700°C and a large amount of tar was formed as a by-product.

~~(1)~~ Gasification furnace

- Spouted bed type

100mm (inner diameter) x 1,500 mm (height)

~~(2)~~ Operating conditions for gasification

530°C, 1 atm.

~~(3)~~ Results of operation

(a) Raw material: FRP (see Table 1) = 100 g/h

(b) $\text{H}_2\text{O}/\text{C} = 8.0$ (molar ratio)

(c) Amount of O_2 supplied

$\text{O}_2/\text{C} = 0.3$ (molar ratio)

(d) Product gas

Flow rate = 101 Nl/h

Composition (vol. %): $H_2=27$, $CO = 28$, $CO_2=31$, $CH_4=11$

(e) Rate of gasification: 64%

Testing Example 3

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49. Using a gasification furnace of the kiln type, gasification was carried out under the conditions given below. In this case, the formation of tar as a by-product was not noted.

(1) Gasification furnace ✓

Kiln type

200 mm (inner diameter) x 1,500 mm (height)

(2) Operating conditions for gasification ✓

780°C, 1 atm.

(3) Results of operation ✓

(a) Raw material: FRP (see Table 1) = 100 g/h

(b) $\text{H}_2\text{O}/\text{C} = 8.0$ (molar ratio)

(c) Amount of O_2 supplied

$$\text{O}_2/\text{C} = 0.3 \text{ (molar ratio)}$$

(d) Product gas

Flow rate = 161 Nl/h

Composition (vol. %): $\text{H}_2 = 47$, $\text{CO} = 29$, $\text{CO}_2 = 23$, $\text{CH}_4 = 0.5$

(e) Rate of gasification: 100%

Comparative Example 2

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~~50.~~ Using a gasification furnace of the kiln type, gasification was carried out under the conditions given below. In this case, a large amount of tar was formed as a by-product.

~~(1)~~ Gasification furnace

Kiln type

200 mm (inner diameter) x 1,500 mm (height)

~~(2)~~ Operating conditions for gasification

560°C, 1 atm.

~~(3)~~ Results of operation

(a) Raw material: FRP (see Table 1) = 100 g/h

(b) $H_2/C = 12.0$ (molar ratio)

(c) Amount of O_2 supplied

$$O_2/C = 0.5 \text{ (molar ratio)}$$

(d) Product gas

Flow rate = 90 NI/h

Composition (vol. %): $H_2 = 25$, $CO = 27$, $CO_2 = 33$, $CH_4 = 11$

(e) Rate of gasification: 56%

Testing Example 4

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ST. Using a gasification furnace of the kiln type, gasification was carried

out under the conditions given below. In this case, a high-quality gas was not

produced, but neither the presence of residual unreacted carbon nor the formation of soot by incomplete combustion was noted.

~~(1)~~ Gasification furnace

Kiln type 200 mm (inner diameter) x 1,500 mm (height)

~~(2)~~ Operating conditions for gasification

790°C, 1 atm.

~~(3)~~ Results of operation

(a) Raw material: FRP (see Table 1) = 100 g/h

(b) $\text{H}_2\text{O}/\text{C} = 3.5$ (molar ratio)

(c) Amount of air supplied

Air = 291 NI/h

$\text{O}_2/\text{C} = 0.75$ (molar ratio)

$\text{O}_2 = 61.2$ NI/h

(d) Product gas

Flow rate = 387 NI/h

Composition (vol. %) : $H_2 = 0.2$, $CO = 3.8$, $CO_2 = 7.7$, $CH_4 = 0.0$, $O_2 = 12.8$, $N_2 = 75.7$

(e) Rate of gasification: 100%

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52. Thus, the first embodiment of the present invention provides a process for the gasification of an organic material which can prevent the presence of residual unreacted carbon and the formation of soot by incomplete combustion during gasification of the organic material and thereby makes it possible to obtain a high-quality gas or recover a gas permitting the recovery of much energy. ✓

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53. Now, the process in accordance with the second embodiment of the present invention will be described hereinbelow with reference to Fig. 1. Fig. 1 is a flow diagram illustrating the process for the gasification of GFRP in accordance with the second embodiment of the present invention. ✓

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54. As shown, this process involves a gasification section 1, a plastic gas decomposition section 2 connected to gasification section 1, a heat recovery section 3, and a gas purification section 4. In the gasification section 1, a first step is carried out in which a GFRP material A that has previously been crushed to ✓

pieces is fed and heated in the presence of oxygen 7 and steam 6 to gasify the plastic component of the GFRP and thereby produce a plastic gas A_1 , and the remaining solid glass fibers A_2 are recovered. In the plastic gas decomposition section 2, a second step is carried out in which the plastic gas A_1 , produced in the first step is introduced and partially oxidized in the presence of additional oxygen 7 and, if necessary, additional steam 6, and the CO and H_2 so produced are recovered.

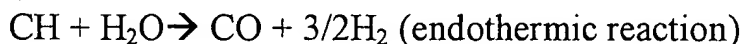
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55. Next, the steps of this gasification process are more specifically explained in the following. A GFRP material A that has previously been crushed to pieces is fed to the gasification section (gasification furnace) 1 where it is heated to a temperature of 650 to 700°C in the presence of oxygen 7 and steam 6 supplied in a sufficient amount to adjust the oxygen partial pressure to 10-15% or less. Thus, the plastic constituting a component of GFRP material A is gasified without forming soot or coking products. The glass fibers A_2 (with a melting point of about 830°C) present in the GFRP remain in the gasification section 1 and are recovered through the discharge orifice thereof (first step). ✓

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56. On the other hand, the plastic gas produced in the first step is introduced into the plastic gas decomposition section (plastic gas decomposition

furnace) 2 where additional oxygen 7 and, if necessary, a sufficient amount of additional steam 6 to adjust the local oxygen partial pressure to 10-15% or less are supplied to plastic gas A₁. As a result, a portion of plastic gas A₁ undergoes the following reaction to produce useful component gases (CO and H₂) without forming soot or coking products.



where CH represents the plastic gas. Moreover, the remainder of plastic gas A₁ is further heated to a temperature of 700 to 1,000°C by the heat Q generated during this reaction and undergoes the following endothermic reaction in the presence of the supplied steam 6.



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57. This endothermic reaction produces highly concentrated useful component gases (CO and H₂) while preventing local heating to high temperatures and thereby suppressing soot formation and coking. The CO and H₂ so produced are passed through the heat recovery section 3, purified in the gas purification column 4, and then recovered by suitable means (second step). ✓

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These CO and H₂ can be utilized as fuel or in methanol synthesis. Since heat absorption takes place during the above-described reactions, the reactions can be allowed to proceed gently by regulating the amount of steam 6 supplied. Thus, highly concentrated CO and H₂ can be efficiently produced at a proper temperature. Now, the apparatus in accordance with the third embodiment of the present invention will be described hereinbelow with reference to Fig. 2. Fig. 2 is a schematic view illustrating the construction of the apparatus for the gasification of GFRP in accordance with the third embodiment.

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As shown, the apparatus is composed of a gasification section (furnace or kiln) 1 consisting of a horizontally disposed rotatable cylindrical structure, a plastic gas decomposition section (furnace) 2 connected to the gasification section (furnace) 1, a heat recovery unit 3, and a gas purification section (column) 4.

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The gasification section (furnace) 1 has a heating zone for receiving a GFRP material A previously crushed to pieces and heating it in the presence of oxygen 7 and steam 6 to gasify the plastic component of the GFRP and thereby produce a plastic gas A₁, and a recovery zone for recovering the glass fibers A₂ remaining after the gasification of the plastic through a discharge orifice. The

plastic gas decomposition section (furnace) 2 consists of a cylindrical or boxlike structure connected to the above-described gasification section (furnace) 1 and disposed vertically, in which the plastic gas A_1 introduced from the gasification section (furnace) 1 is partially oxidized in the presence of additional oxygen 7 and, if necessary, additional steam 6. The heat recovery section 3 is a device for recovering heat from the gas produced in the plastic gas decomposition section (furnace) 2, and the gas cooled in the heat recovery section 3 is purified in the gas purification section (column) 4.

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61. Next, the procedure for gasification using this gasification apparatus is described in greater detail. ✓

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62. First of all, a GFRP material A that has previously been crushed to pieces is fed to the gasification section (rotating furnace) 1. In the gasification section 1, GFRP material A is heated to a temperature of 650 to 700°C in the presence of oxygen 7 and steam 6. Thus, the plastic constituting a component of the GFRP is gasified to produce a plastic gas A_1 . The glass fibers (with a melting point of about 830°C) present in the GFRP remain in the gasification section 1, move forward with the rotation of the gasification section 1, and are recovered through a discharge orifice 5. ✓

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On the other hand, plastic gas A_1 is introduced into the plastic gas decomposition section (furnace) 2. To this decomposition section 2 are supplied additional oxygen 7 and, if necessary, an appropriate amount of additional steam 6. As a result, a portion of plastic gas A_1 undergoes the following reaction:



Thus, the portion of plastic gas A_1 is oxidized (or burned) at a temperature of about 700 to 1,000°C to generate heat Q . The resulting gas is introduced into a heat recovery section 3 where heat Q is recovered.

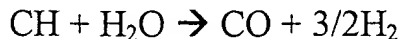
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In the presence of additional oxygen 7 and, if necessary, an appropriate amount of additional steam 6, another portion of plastic gas A_1 undergoes the following reaction to produce CO and H_2 .



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Moreover, the remainder of plastic gas A_1 is heated to a temperature of 700 to 1,000°C by the generated heat Q and undergoes the following reaction in the presence of additional steam 6 to produce highly concentrated useful component gases (CO and H_2).



The CO and H₂ so produced, together with other combustion gases, are introduced into the heat recovery unit 3 where they are cooled to recover the heat. Then, they are introduced into the gas purification section 4 where harmful materials such as SO₂ and HCl are absorbed and separated. The CO and H₂ so purified are recovered and utilized as fuel or in methanol synthesis.

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66. As described above, heat absorption takes place as a result of the combined use of oxygen 7 and steam 6 in gasification section 1 and plastic gas decomposition section 2. Accordingly, by properly regulating the amount of steam 6 and thereby allowing the reactions to proceed gently, the gasification of GFRP can be effected at a proper temperature to recover the glass fibers and the generated heat efficiently. Moreover, highly concentrated CO and H₂ can be efficiently produced at a proper temperature.

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67. Now, the effects produced by the second and third embodiments of the present invention will be demonstrated by the following Testing Examples 5 and 6.

Testing Example 5

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68. A GFRP for use in boats having the analytical values given below was cut into ~~about mm~~ cubes *with a size of about 5 mm* and this GFRP material A was gasified according to the

flow diagram of Fig. 1. The resulting gas was subjected to heat recovery and then purified to obtain a synthesis gas. Both the gasification section 1 and the plastic gas decomposition section 2 comprised quartz tubes having an inner diameter of 5 cm, and the overall length of these quartz tubes was fixed at 2 m. The temperature of the gasification section 1 could be varied between 600°C and 900°C, and the temperature of the plastic gas decomposition section 2 between 600°C and 1,000°C. GFRP material A was fed to the gasification section 1 at a constant rate of 0.5 g/min.

(Analytical values of GFRP)

C: 50.4 wt. %

H: 4.4 wt. %

O: 7.5 wt. %

Water: 0.0 wt. %

Ash (including glass fibers): 37.7 wt. %

071
~~69~~. The operating conditions of the gasification section 1 and the plastic gas decomposition section 2 were set as shown in Table 1. Quartz wool or a filter

was disposed at the inlet of heat recovery unit 3 to collect any soot or tar in the product gas. After a predetermined testing time (about 35 minutes), the glass fibers were removed, examined by visual observation, and analyzed for unburned carbon. The results thus obtained are shown in Table 2.

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20.

Table 2

✓

| RUN No. | First step (gasification section) | | | | Second step (plastic gas decomposition section) | | | *Rate of Gasification (wt%) |
|------------|--------------------------------------|--------------|--------------------|------------------|---|--------------------|------------------|-----------------------------------|
| | Feed rate of GFRP (g/min.) | Temp (°C) | Oxygen (l/min.) | Steam (g/min) | Temp. (°C) | Oxygen (l/min.) | Steam (g/min) | |
| 1 | 0.5 | 600 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 86 |
| 2 | 0.5 | 650 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 99 |
| 3 | 0.5 | 700 | 0.12 | 2.0 | 700 | 0.13 | 0.5 | 99 |
| 4 | 0.5 | 700 | 0.12 | 2.0 | 850 | 0.13 | 0.5 | 100 |
| 5 | 0.5 | 700 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 100 |
| 6 | 0.5 | 700 | 0.12 | 2.0 | 1,000 | 0.13 | 0.0 | 98 |
| 7 | 0.5 | 700 | 0.12 | 2.0 | 1,000 | 0.0 | 0.0 | 75 |
| 8 | 0.5 | 700 | 0.12 | 2.0 | 1,000 | 0.0 | 0.0 | 70 |
| 9 | 0.5 | 750 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 99 |
| 10 | 0.5 | 800 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 85 |
| 11 | 0.5 | 900 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 83 |
| 12 | 0.5 | 1,000 | 0.12 | 2.0 | 1,000 | 0.13 | 0.5 | 83 |
| 13 | 0.5 | 700 | 0.12 | 0.0 | 1,000 | 0.13 | 0.5 | 86 |
| 14 | 0.5 | 700 | 0.0 | 0.0 | 1,000 | 0.13 | 0.5 | 69 |
| 15 | 0.5 | 700 | 0.0 | 2.0 | 1,000 | 0.13 | 0.5 | 70 |

073
H.

Table 2 (Continuation)

| RUN No. | Composition of product gas (vol. %) | | | Coking products or unburned components in glass fibers O: Absent x: Present | Tar or soot in product gas Δ: Some O: None x: Much | Overall Evaluation |
|------------|---|----|-----------------|---|--|-----------------------|
| | H ₂ | CO | CO ₂ | | | |
| 1 | 1 | 66 | 33 | x | O | x |
| 2 | 3 | 64 | 33 | O | O | O |
| 3 | 5 | 60 | 35 | O | O | O |
| 4 | 20 | 50 | 30 | O | O | O |
| 5 | 40 | 25 | 35 | O | O | O |
| 6 | 39 | 24 | 37 | O | Δ | O |
| 7 | 42 | 40 | 18 | O | x | x |
| 8 | 60 | 22 | 18 | O | O | O |
| 9 | 42 | 25 | 33 | O | O | O |
| 10 | 44 | 24 | 32 | x | x | x |
| 11 | 46 | 22 | 32 | x | x | x |
| 12 | 47 | 21 | 32 | x | x | x |
| 13 | 43 | 41 | 16 | x | x | x |
| 14 | 41 | 41 | 18 | x | x | x |
| 15 | 41 | 44 | 15 | x | x | x |

(*) The percentage of the carbon in the GFRP material which was converted into CO and CO₂

Testing Example 6

074
72. An example of the apparatus for the gasification of GFRP in accordance with the third embodiment of the present invention is presented. This apparatus has the same construction as that illustrated in Fig. 2. The specifications of several components of this apparatus, its operating conditions, and the results of operation are given below. The GFRP material used was the same as that described in Testing Example 5.

075 (Specifications):

72. Gasification section or furnace 1: 150 mm (diameter) x 500 mm (length). Rotational speed of gasification section 1: 6 rpm. Plastic gas decomposition section or furnace 2: 200 mm (diameter) x 1,500 mm (length)

076 (Operating conditions):

74. Temperature of gasification section 1: 710°C. Amount of steam supplied to gasification section 1

- 4.4 Nm³/h

75. Amount of oxygen supplied to gasification section 1: 0.9 Nm³/h

~~0.9 Nm³/h~~ ✓

~~76.~~ Temperature of plastic gas decomposition section 2: 98°C. Amount of oxygen supplied to plastic gas decomposition section 2: 1.0 Nm³/h

077. (Results of operation) ;

Flow rate of product gas: 15.3 Nm³/h

~~077.~~ Composition of product gas (vol. %): H₂ = 38.0, CO = 41.0, CO₂ = 21.0. (The H₂ and CO concentrations are so high that the product gas can be satisfactorily used as a gas for the production of methanol.) ✓

~~078~~ Rate of gasification (i.e., the percentage of the carbon in GFRP which was converted into CO and CO₂): 100%. Residue: Only white glass fibers containing no unreacted carbon components or coking products (continuously recovered). ~~078~~ Thus, according to the second and third embodiments of the present invention, a GFRP material is gasified in the gasification section (or gasification furnace) in the presence of oxygen and an appropriate amount of steam, so that only the plastic component of the GFRP is gasified and the remaining glass fibers can be recovered. Then, the resulting plastic gas A₁ is decomposed in the plastic gas decomposition section (or plastic gas decomposition furnace) under mild ✓

conditions, so that a synthesis can be obtained without causing damage to the walls of the furnace owing to high-temperature combustion as was usual with the prior art.

Ø 79. Now, the process in accordance with the fourth embodiment of the present invention will be described hereinbelow with reference to Fig. 3. Fig. 3 is a flow diagram illustrating the process for the gasification of GFRP in accordance with the fourth embodiment. ✓

Ø 80. As shown, this process involves a gasification section 21, a combustion section 22 connected to the gasification section 21, and a heat recovery section 23 connected to a combustion section 22. In the gasification section 21, a first step is carried out in which a GFRP material A that has previously been crushed to pieces is fed and heated in the presence of air 27 and steam 26 to gasify the plastic component of the GFRP and thereby produce a plastic gas A_1 , and the remaining solid glass fibers A_2 are recovered. In the combustion section 22, a second step is carried out in which the plastic gas A_1 produced in the first step is introduced and burned in the presence of additional air 27 and, if necessary, additional steam 26, and the heat so generated is recovered in the heat recovery ✓

section 23. In Fig. 3, reference numeral 24 designates a flow path of exhaust gas comprising CO₂, H₂O, N₂ and the like.

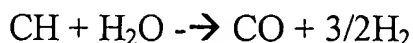
Ø 81. Next, the steps of this gasification process are more specifically explained in the following. A GFRP material A that has previously been crushed to pieces is fed to the gasification section (gasification furnace) 21 where it is heated to a temperature of 650 to 750°C in the presence of appropriate amounts of air 27 and steam 26. Thus, the plastic constituting a component of GFRP material A is gasified. The glass fibers A₂ (with a melting point of about 830°C) present in GFRP material A remain in the gasification section 21 and are recovered through the discharge orifice thereof (first step). ✓

Ø 82. On the other hand, the plastic gas A₁, produced in the first step, is then introduced into the combustion section (combustion furnace) 22 where additional air 27 and, if necessary, an appropriate amount of additional steam 26 are supplied to plastic gas A₁. As a result, plastic gas A₁ undergoes the following reaction: ✓



where CH represents the plastic gas. Thus, plastic gas A₁ is oxidized (or burned) at a temperature of about 700 to 1,000°C to generate heat Q. This heat Q is recovered in the heat recovery section 23 (second step).

Ø 83. When GFRP material A is heated in the gasification section 21 and plastic gas A₁ is burned in the combustion section 22, the presence of an appropriate amount of steam 26 induces heat absorption as a result of the following reaction:



Ø 84. Since this causes the reactions to proceed gently, the local production of high temperatures is suppressed during heating of the GFRP in the presence of oxygen in air or combustion of the plastic gas in the presence of oxygen in air, so that coking phenomena can be prevented.

Ø 85. Now, the apparatus in accordance with the fifth embodiment of the present invention will be described hereinbelow with reference to Fig. 4. Fig. 4 is a schematic view illustrating the construction of the apparatus for the gasification of GFRP^g in accordance with the fifth embodiment.

Ø 86. As shown, the apparatus is composed of a gasification section (furnace or kiln) 21 consisting of a horizontally disposed rotatable cylindrical structure, a plastic gas combustion section (furnace) 22 connected to gasification section^{e 21} 21, and a heat recovery section 23 connected to the combustion section 22.

Ø 87. The gasification section 21 has a heating zone for receiving a GFRP material A previously crushed to pieces and heating it in the presence of oxygen 27 and steam 26 to gasify the plastic component of the GFRP and thereby produce a plastic gas A₁, and a recovery zone for recovering the glass fibers A₂ remaining after the gasification of the plastic through a discharge orifice 25. The combustion section 22 consists of a cylindrical or box-like structure connected to the above-described gasification section 21 and disposed vertically, in which the plastic gas A₁ introduced from the gasification section 1 is burned in the presence of additional air 27 and, if necessary, additional steam 26. The heat recovery section 23 is an apparatus for recovering the heat generated in combustion section 22. ✓

Ø 88. Next, the procedure for gasification using this gasification apparatus is described in greater detail. ✓

Ø 89. First of all, a GFRP material A that has previously been crushed to pieces is fed to the rotating gasification section 21. In gasification section 21, GFRP material A is heated to a temperature of 650 to 750°C in the presence of air 27 and steam 26. Thus, the plastic constituting a component of the GFRP is gasified to produce a plastic gas A₁. The glass fibers A₂ (with a melting point of ✓

about 830°C) present in the GFRP remain in the gasification section 21, move forward with the rotation of the gasification section 21, and are recovered through a discharge orifice ~~25~~ 25. ✓

Ø 90. On the other hand, plastic gas A₁ is introduced into the combustion section 22 where additional air 27 and, if necessary, an appropriate amount of additional steam 26 are supplied to plastic gas A₁. As a result, plastic gas A₁ undergoes the following reaction: ✓



Thus, plastic gas A₁ is oxidized (or burned) at a temperature of about 700 to 1,000°C to generate heat Q. The resulting combustion gas is introduced into a heat recovery section (such as a heat exchanger) 23 where heat Q is recovered.

Ø 91. As described above, heat absorption takes place as a result of the combined use of oxygen 27 and steam 26 in the gasification section 21 and the combustion section 22. Accordingly, by properly regulating the amount of steam 26 and thereby allowing the reactions to proceed gently, the gasification of GFRP can be effected at a proper temperature to recover the glass fibers and the generated heat efficiently. ✓

Q 92. Now, the effects produced by the fourth and fifth embodiments of the present invention will be demonstrated by ^g2 the following Testing Examples 7 and 8.

Testing Example 7

Q 93. A GFRP for use in boats having the analytical values given below was cut into about 5 mm cubes. This GFRP material A was gasified according to the flow diagram of Fig. 3 and the heat so generated was recovered. Both the gasification section 21 and the combustion section 22 comprised quartz tubes having an inner diameter of 5 cm, and the overall length of these quartz tubes was fixed at 2 m. The temperature of the gasification section 21 could be varied between 600°C and 900°C, and the temperature of the combustion section 22 between 700°C and 1,000°C. GFRP material A was fed to the gasification section 21 at a constant rate of 0.5 g/min.

(Analytical values of GFRP)

C: 50.4 wt. %

H: 4.4 wt. %

O: 7.5 wt%

Water: 0.0 wt. %

Ash (including glass fibers): 37.7 wt. %

0 94. The operating conditions of the gasification section 21 and the combustion section 22 were set as shown in Table 3. Quartz wool or a filter was disposed at the inlet of heat recovery section 23 to collect any soot or tar in the product gas. After a predetermined testing time (about 35 minutes), the glass fibers were removed, examined by visual observation, and analyzed for unburned carbon. The results thus obtained are shown in Table 3. ✓

Ø 95.

Table 3



| RUN No. | First step (gasification section) | | | | Second Step (Combustion section) | | |
|------------|--------------------------------------|---------------|----------------|------------------|-------------------------------------|----------------|------------------|
| | Feed Rate of GFRP (g/min) | Temp. (°C) | Air (l/min) | Steam (g/min) | Temp. (°C) | Air (l/min) | Steam (g/min) |
| 1 | 0.5 | 600 | 1.2 | 2.0 | 600 | 2.4 | 0.0 |
| 2 | 0.5 | 650 | 1.2 | 2.0 | 650 | 2.4 | 0.0 |
| 3 | 0.5 | 700 | 1.2 | 2.0 | 700 | 2.4 | 0.0 |
| 4 | 0.5 | 700 | 1.2 | 2.0 | 1,000 | 2.4 | 0.0 |
| 5 | 0.5 | 700 | 1.2 | 2.0 | 1,000 | 2.4 | 0.5 |
| 6 | 0.5 | 700 | 1.2 | 2.0 | 850 | 2.4 | 0.0 |
| 7 | 0.5 | 700 | 1.2 | 2.0 | 850 | 2.4 | 0.5 |
| 8 | 0.5 | 750 | 1.2 | 2.0 | 750 | 2.4 | 0.5 |
| 9 | 0.5 | 800 | 1.2 | 2.0 | 800 | 2.4 | 0.5 |
| 10 | 0.5 | 900 | 1.2 | 2.0 | 900 | 2.4 | 0.5 |
| 11 | 0.5 | 700 | 0.0 | 0.0 | 700 | 2.4 | 0.5 |
| 12 | 0.5 | 700 | 0.0 | 0.0 | 700 | 2.4 | 0.5 |
| 13 | 0.5 | 700 | 2.0 | 2.0 | 700 | 2.4 | 0.5 |

096.

Table 3 (Continuation)

✓

| RUN No. | *Rate of Gasification (wt %) | Coking products Or unburned components in glass fibers O: Absent x: Present | Tar or soot in product gas O: Absent x: Present |
|------------|------------------------------------|--|--|
| 1 | 85 | x | O |
| 2 | 98 | O | O |
| 3 | 99 | O | O |
| 4 | 99 | O | O |
| 5 | 100 | O | O |
| 6 | 99 | O | O |
| 7 | 100 | O | O |
| 8 | 100 | O | O |
| 9 | 86 | x | x |
| 10 | 90 | x | x |
| 11 | 83 | x | x |
| 12 | 60 | x | x |
| 13 | 72 | x | x |

(*) The percentage of the carbon in the GFRP material which was converted into CO and CO₂

Testing Example 8

097. An example of the apparatus for the gasification of GFRP in accordance with the fifth embodiment of the present invention is presented. This apparatus has the same construction as that illustrated in Fig. 4. The specifications of several components of this apparatus, its operating conditions, and the results of

✓

operation are given below. The GFRP material used was the same as that described in Testing Example 7.

Ø 98. (Specifications) ✓

Gasification section ~~(furnace)~~ ^{section} 21: 150 mm (diameter) x 500 mm (length) ✓

(length) ✓

Rotational speed of the gasification ~~furnace~~ ^{section} 21: 6 rpm

Combustion section ~~(furnace)~~ ^{section} 22: 200 mm (diameter) x 1,500 mm (length)

(length) ✓

(Operating conditions)

Ø 99. Temperature of the gasification ~~furnace~~ ^{section} 21: 700°C. Amount of steam supplied to gasification furnace 21: ✓

3.6 Nm³/h

Amount of air supplied to the gasification section 21: 5.0 Nm³/h

Temperature of the ~~(plastic gas decomposition section)~~ ^{combustion section 22} 22: 990°C ✓

Amount of air supplied to the combustion ~~furnace~~ ^{section} 22: 5.4 Nm³/h

(Results of operation)

Flow rate of product gas: 15.3 Nm³/h

Composition of product gas (vol. %): CO₂ = 21.7, N₂ = 79.3

Rate of gasification (i.e., the percentage of the carbon in GFRP which was converted into CO₂): 100%

100. Residue: Only white glass fibers containing no unreacted carbon components or coking products (continuously recovered).

101. Thus, according to the fourth and fifth embodiments of the present invention, a GFRP material is gasified in the gasification section (or gasification furnace) in the presence of air and an appropriate amount of steam, so that only the plastic component of the GFRP is gasified and the remaining glass fibers can be recovered. Then, the resulting plastic gas is burned in the combustion section (or combustion furnace) under mild conditions, so that heat recovery can be achieved without causing damage to the walls of the furnace owing to high-temperature combustion as was usual with the prior art.

102. The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure

from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.